Journal of Cleaner Production 185 (2018) 852–859

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Pistachio (*Pistachia vera*) wastes valorization: Enhancement of biodiesel oxidation stability using hull extracts of different varieties

Mitra Ahanchi [a], Meisam Tabatabaei [b, c, *], Mortaza Aghbashlo [d, **], Keramatollah Rezaei [a], Ahmad Farhad Talebi [e], Akram Ghaffari [c], Benyamin Khoshnevisan [b, d], Zahra Khounani [b, c]

[a] Department of Food Science and Engineering, Faculty of Agricultural Engineering and Technology, University of Tehran, Karaj, Iran
[b] Biofuel Research Team (BRTeam), Karaj, Iran
[c] Agricultural Biotechnology Institute of Iran (ABRII), Agricultural Research, Education, and Extension Organization (AREEO), 31535-1897 Karaj, Iran
[d] Department of Agricultural Machinery Engineering, Faculty of Agricultural Engineering and Technology, College of Agriculture & Natural Resources, University of Tehran, Karaj, Iran
[e] Genetic Department, Faculty of Biotechnology, Semnan University, Semnan, 35131-19111, Iran

A R T I C L E I N F O

Article history:
Received 7 November 2017
Received in revised form
11 February 2018
Accepted 8 March 2018
Available online 9 March 2018

Keywords:
Biodiesel
Oxidative degradation
Propyl gallate
Health hazards
Pistachio wastes valorization
Natural antioxidant

A B S T R A C T

Biodiesel degradation through autoxidation radical chain reactions adversely affects long-term storage stability, high thermal oxidation stability, and consequently biodiesel consumers' acceptance. Propyl gallate, the most promising synthetic antioxidant, is widely used to address this challenge. However, the application of this synthetic antioxidant is associated with health concerns such as risk of brain tumors as proposed by the National Toxicology Program (U.S. Department of Health and Human Services). Herein, the application of a naturally-originated alternative to propyl gallate, i.e., pistachio hull extract in canola biodiesel was investigated from technical and environmental viewpoints. According to the results achieved, a concentration of 2500 ppm of the bio-antioxidant and 250 ppm of the synthetic antioxidant was needed to improve the induction period of the investigated biodiesel from 1.53 h to above 3 h as required by ASTM D6751-12 specification for biodiesel oxidation stability. In spite of the fact that the higher concentration of the bio-antioxidant was required, its application would be justified by the probable health hazards of its synthetic counterparts. On the other hand, 23% of the global biodiesel production takes place in top pistachio producing countries where a huge amount of pistachio fresh hulls are generated. Therefore, valorization of this considerable agro-waste stream into a natural antioxidant, i.e., pistachio hull extract, seems to be a promising strategy to enhance the favorable environmental and health aspects of biodiesel. In addition, life cycle assessment revealed that the production and application of the bio-antioxidant were favorable from the climate change and human health perspectives compared with propyl gallate.

1. Introduction

Biodiesel, short-chain alkyl (methyl or ethyl) esters, is a nonpetroleum-based diesel fuel and is generally produced through the transesterification of vegetable/algal oils and animal fats (Talebi et al., 2015). Short-term storage stability as well as short thermal oxidation stability (OS) are critical attributes of biodiesel and its blends which could influence the widespread marketability of this green energy carriers (Agarwal et al., 2015). In fact, owing to the presence of unsaturated fatty acids (FAs) in oil feedstocks used to produce biodiesel, the fuel undergoes oxidative degradation during its storage and commercialization (de Sousa et al., 2014). Mittelbach and Schober (2003) claimed that FA derivatives such as fatty acid methyl esters (FAMEs) (also known as biodiesel) are more susceptible to oxidative degradation compared with mineral diesel fuel.

Autoxidation (degradation) of biodiesel when exposed to specific conditions during storage adversely affects fuel properties

* Corresponding author. Biofuel Research Team (BRTeam), Microbial Biotechnology Department Agricultural Biotechnology Research Institute of Iran (ABRII) Karaj, Iran.
** Corresponding author. Faculty of Agricultural Engineering and Technology, University of Tehran, Karaj, Iran.
E-mail addresses: meisam_tabatabaei@abrii.ac.ir (M. Tabatabaei), maghbashlo@ut.ac.ir (M. Aghbashlo).

https://doi.org/10.1016/j.jclepro.2018.03.089

such as Kinematic viscosity, acid value, and peroxide value (Dunn, 2005; Kumar et al., 2018). In fact, the generation of free radicals plays a key role in the progression of destructive reactions in biodiesel (Christensen and McCormick, 2014). Kamal-Eldin and Pokorny (2005) summarized the oxidation of polyunsaturated fatty acid esters in biodiesel in different phases: the free radicals are formed in the first phase (i.e., the induction period; IP) but interestingly they react predominantly with antioxidants if present, rather than the biodiesel itself. Consequently, the chemical composition of the fuel is not significantly impacted as long as the antioxidant molecules are sufficiently present. Having exhausted the antioxidant compounds, the reaction of oxygen with the fuel takes place, leading to the formation of peroxides, acids, and the other degradation products (Pölczmann et al., 2016). As mentioned earlier, this phenomenon in turn heavily jeopardizes fuel quality parameters.

The oxidation process in biodiesel can be prevented or slowed down by adding various synthetic or natural antioxidants. Du Plessis et al. (1985) pioneered the studies on storage stability of biodiesel. Their results confirmed that keeping biodiesel at 20 °C in closed containers or storing it after the addition of an antioxidant could stabilize the fuel structure. In a comprehensive study, Serrano et al. (2013) compared the efficiency of three synthetic and one natural antioxidants for improving the OS of biodiesel produced from soybean, rapeseed, sun flower, and palm oils. They concluded that the synthetic antioxidant propyl gallate (PG) resulted in the best oxidative stability. Similar observations concerning the superiority of synthetic antioxidants over natural antioxidants have been reported in other investigations (Dunn, 2005).

In spite of the better performance of synthetic antioxidants, natural antioxidants are regarded as a better choice for improving biodiesel OS due to their biodegradability and non-toxicity. For instance, a study conducted by the National Toxicology Program (U.S. Department of Health and Human Services) claimed an association between PG and tumors in male rats and rare brain tumors in female rats (Levy, 1982). Although these findings did not establish a clear link between PG and cancer, but they raised serious concern about the safety aspects of this chemical. This has sparked interest in the development of natural antioxidants for biodiesel preservation. For instance, Botella et al. (2014) used 4-allyl-2,6-dimethoxyphenol and catechol as antioxidant in rapeseed and soybean biodiesel and reported a significant enhancement in the OS of both samples with a higher effect for catechol. In another study, curcumin and β-carotene were added into soybean biodiesel for controlling its oxidative process (de Sousa et al., 2014). Curcumin increased the IP of biodiesel by 83% whereas β-carotene acted as a pro-oxidant and decreased the IP of the investigated biodiesel. In a different study, Machado et al. (2014) suggested that a 50% difference observed in reactivity towards oxidation of moringa and passion fruit oils was a result of a higher concentration of natural antioxidant agents in moringa oil. Having scrutinized the available literature, one could comprehend that natural sources of antioxidants beating synthetic ones are yet to be introduced.

Pistachio (*Pistacia vera*) is a popular fruit tree known as the king of nuts in terms of its nutrition value and price. Its total world trade exceeds 2526 million USD, approx. 50% of which is contributed by Iran (FAO, 2016). One of the main waste feedstocks associated with pistachio is its soft cellulosic hulls (1% protein, 55% reducing sugars) produced during the dehulling process (Goli et al., 2005). Currently, just a small portion of these pistachio fresh hulls are consumed as animal feed and the rest of the biomass is disposed of as agricultural wastes in the environmental (Bohluli, 2006). It should be noted that the tannins and polyphenolic compounds present in the hulls reduce its acceptance and digestibility as animal feed. While, these compounds available in the pistachio hull extract (PHE) could potentially be powerful antioxidants to scavenge free radicals (Goli et al., 2005). In a study, antioxidant activity and total phenolic compounds of PHE extracted by various methods (solvent and ultrasound-assisted) were determined by Goli et al. (2005). They reported a significant improvement in preventing soybean oil deterioration during heating (oven test method) in the presence of PHE. Rajaei et al. (2010) also studied the antioxidant activities of crude and purified green hull extracts of pistachio (Ahmad-Aghaei variety) using the 2,2′-azino-bis-3-ethylbenzthiazoline-6-sulphonic acid (ABTS), DPPH, and β-carotene bleaching methods. They reported a concentration-dependent antioxidative capacity for both the crude and purified PHE.

It should be noted that the main aim of using biodiesel is attributed to its impacts on reducing environmental emissions and the consequent positive impacts on the ecosystem and human health. On such basis, it is of critical significance to strive to enhance such features and avoid the introduction of any compounds including synthetic antioxidants such as PG, which could potentially jeopardize the health benefits of the alternative fuel. Therefore, the present study was set to valorize pistachio soft hulls by developing new natural antioxidants for biodiesel. To achieve that, the PHEs of different pistachio varieties, i.e., Ahmad-Aghaei, Akbari, Fandoghi, and Kalle-Ghuchi were obtained and their antioxidant activities were compared with PG as the most promising synthetic antioxidants. Given the health risks of PG and the fact that pistachio hulls end up as agricultural wastes at the moment and that they can be obtained as an inexpensive and easily available source of natural antioxidant, the findings of the present study could be of wide interest to the biodiesel industry worldwide.

2. Materials and methods

2.1. Plant materials and chemicals

Four major commercial Iranian pistachio varieties (i.e., Ahmad-Aghaei, Akbari, Fandoghi, and Kalle-Ghuchi) were investigated in the present study. The samples were randomly obtained during the pistachio harvesting season (i.e., in September). Plant materials, i.e., pistachios including fresh hulls were harvested from pistachio farms located in the Abozeyd'abad region, Kashan, Iran. Due to the rapid perishability of soft hulls, pistachios were quickly dehulled. Hulls were cold air-dried in the dark for 48 h. Dried hulls were then ground to fine powder (diameter <1 mm) using an electric mill. The powder was then sieved using a laboratory 18-mesh sieve and was subsequently weighted and stored until the extraction process. All chemicals and solvents including n-hexane, acetic acid, chloroform, potassium hydroxide, methanol, sulfuric acid, sodium chloride, and PG were of analytical grade and were purchased from Sigma (Deisenhofen, Germany).

2.2. Oil extraction procedure from pistachio soft hulls

To extract total oil and phenolic compounds from the pistachio soft hulls, n-hexane was used as solvent. Ten g of the dried hull powders were extracted using 40 g of the solvent. The powder-solvent was mixed using a shaker at room temperature for 24 h. After the completion of the extraction, hexane was recycled. Moreover, the oil solution was filtered to remove the scum and hull particles. In order to improve the efficiency of the extraction, the residues were extracted again with 80 ml of fresh n-hexane for three times. Finally, the solvent was recycled under vacuum at room temperature using a rotary evaporator. The wet oil content was determined gravimetrically and the purified PHEs were placed

in dark color glass-containers and were refrigerated to prevent chemical and physical changes.

2.3. Determination of oils indices and properties

The resulting PHE samples were further analyzed. The acid value (AV) representing the amount of free fatty acid (FFA) in the PHE was determined according to the Cd 3d-63 (AOCS, 1999). Peroxide value (PV) was measured spectrophotometrically according to the thiocyanate method as described by Shantha and Decker (1994). Color of the obtained PHEs were determined using Lovibond tintometer (Beijing, China) according to the standard method of Codex Alimentarius Commission (Cornelius, 1977). Oil density was also determined using a similar standard method. Apparent viscosity of the PHEs obtained from different pistachio varieties was measured using a rotational viscometer (LVDV-II Pro, Brookfield Engineering Inc., USA) with a cylindrical LV spindle (model LV-4) at room temperature.

2.4. Determination of FA composition of PHEs

First, the FAMEs of the PHEs were prepared according to the method previously described by Metcalfe et al. (1966). Briefly, around 0.04 g of the extract was weighed in a glass tube. Subsequently, 5.0 ml of 2.0% (w/v) methanolic sodium hydroxide was added to the sample followed by incubation in boiling water for 10 min. After cooled to room temperature, 2.20 ml boron trifluoride (BF_3) was added to the sample and was boiled again for 3 min. Having cooled the sample, 1.5 ml of hexane and 1.0 ml of saturated NaCl solution were added and the tubes were shaken vigorously and then left to stand at room temperature for 3 min. Finally, the upper layer was transferred to a small vial and stored at 0 °C until analyzed.

FA composition of the extracted oils were then determined by a Varian CP-3800 GC gas chromatograph (GC) (Varian Inc., Palo Alto, CA) equipped with a CP-Sill 88 fused silica column (0.25 mm ID × 100 m long × 0.25 μm film thickness). The oven temperature was set at 130 °C and was held at that temperature for 4 min, then programmed to increase to 180 °C at a rate of 5 °C/min, and was kept at this temperature for 8 min. Finally, the oven temperature was programmed to rise from 180 to 220 °C at the rate of 4 °C/min under the following conditions: helium as the carrier gas (1 mL/min), split ratio of 20:1, and flame ionization detector (FID) temperature of 280 °C. The FAMEs were identified and quantified by comparing their retention times with those of the standards.

2.5. Biodiesel production

Biodiesel was produced through the transesterification reaction from canola oil with methanol and in the presence of an alkali catalyst (KOH) in a stirred tank reactor at 60 °C for 1 h. Upon the completion of the reaction, the mixture was allowed to settle for 1 h and the glycerol phase was removed. Finally, the crude biodiesel was washed and oven dried. In order to determine the properties of the produced canola biodiesel (CBD), “Biodiesel Analyzer© Ver. 1.1” (available on "www.brteam.ir/biodieselanalyzer") was used (Talebi et al., 2013, 2014). The properties included oxidation stability (OS), allylic position equivalent (APE), bis-allylic position equivalent (BAPE), long chain saturated factor (LCSF), cold filter plugging point (CFPP), cloud point (CP), pour point (PP), saponification value (SV), iodine value (IV), Cetane number (CN), degree of unsaturation (DU), higher heating value (HHV), kinematic viscosity (ν), and density (ρ). Moreover, to investigate possible changes, the properties of CBD containing the highest concentration of the PHE (possessing the highest OS) were also determined.

2.6. Thermal oxidation stability analysis

The OS of the four PHEs were compared based on ASTM D6751-12 (USA) standard by measuring the IP using a Model 743 Rancimat (Metrohm AG, Herisau, Switzerland) (Botella et al., 2014). An air flow of 20 L/h was used and the temperature of the heating block was set at 110 °C. Subsequently, the extract with the highest OS was added to CBD at different concentrations (i.e., 1000, 2500, 5000, and 10000 ppm). Moreover, a synthetic antioxidant commonly used in biodiesel, i.e., PG, was also added to CBD at 250, 500, 750, and 1000 ppm. PG was dissolved in biodiesel by the means of sonication for 30 min at 40 °C using an ultrasonic bath. A neat CBD sample without any additives was considered as control. The OS was presented as the duration of the IP (h) and the effectiveness of the treatments were expressed as a stabilization factor (Eq. (1)):

$$F = IP_x / IP_0 \tag{1}$$

where IP_X is the IP in the presence of the antioxidant, and IP_0 is the IP in the absence of the antioxidant.

2.7. Statistical analysis

Different parameters were reported as the mean ± standard deviation (x ± S.D.). Analysis of variance (ANOVA) was performed using Statistix 8 software. The comparison of means was conducted using least significant difference (LSD) test at the confidence level of 95%. Further analyses were performed using Microsoft Excel 2010. All the experiments were carried out in triplicate.

2.8. Environmental considerations

The production and consumption of new products, especially those produced to replace functionally similar products, without considering their sustainability issues cannot be recommended (Rajaeifar et al., 2017; Mandegari et al., 2017b). In better words, apart from the technological and technical issues considered herein, sustainability considerations should also be taken into account (Veleva and Ellenbecker, 2001; United Nations Environment Programme, 2009; Khoshnevisan et al., 2018). In this context, life cycle assessment (LCA) could be a valuable tool. LCA, based on the definition presented by ISO 14040 (ISO, 2006) is a scientific approach which deals with the environmental consequences of a given product during its entire life (JRC, 2010). More specifically, LCA aims at achieving more sustainable production and consumption patterns using its structured, comprehensive, and internationally-standardized method (JRC, 2010; Farzad et al., 2017; Khoshnevisan et al., 2017; Yunos et al., 2017). Accordingly, in the present study, two scenarios were defined and compared using the LCA approach. The scenarios developed were as follows:

Scenario one (Sc-1): CBD supplemented with PHE.

Scenario two (Sc-2): CBD supplemented with PG.

To correctly carry out the LCA of the above-mentioned scenarios, ISO 14040 (ISO, 2006) guidelines were followed including goal definition, life cycle inventory (LCI), life cycle impact assessment (LCIA), and interpretation of the obtained results. The goal was to compare the environmental consequences of the production and application of the two different antioxidants as biodiesel additives. A cradle to gate system boundary was chosen meaning that the current study considered all operations from the extraction of raw materials to the production of the final products (i.e., biodiesel supplemented with PHEs or PG) (Fig. 1). The functional unit (FU), defined as quantified performance of a product system for use as a reference unit (Cavalett et al., 2013; Mandegari et al., 2017a), was selected to be 1 kg of biodiesel supplemented with PHEs or PG.

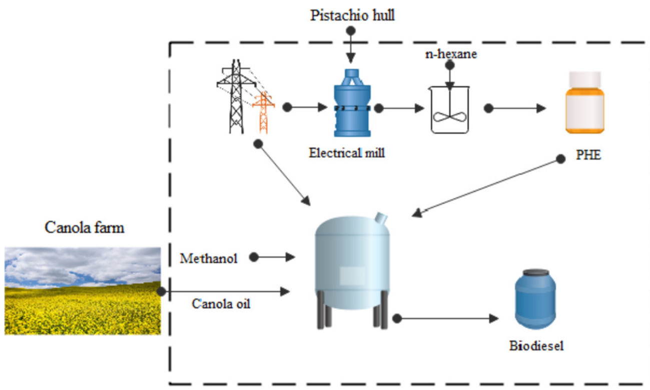

Fig. 1. System boundary related to CBD supplemented with PHE.

The inventory data were compiled based on two types of data set. The background data, i.e., the data related to the production of the employed inputs and energy carriers, were taken from Ecoinvent database and the data from the foreground system, i.e., the data related to the amount materials and energy carrier used, were collected from the lab experiments. The inventory data were modeled using SimaPro 8.3 and IMPACT 2002 + method. This method was used due to its frequent use in similar studies (Melamu and Von Blottnitz, 2011; Cavalett et al., 2013; Rajaeifar et al., 2016) and covering a wide range of impact and damage categories (Jolliet et al., 2003; Rafiee et al., 2016).

3. Results and discussion

3.1. Oil indices and properties of PHEs

The oil contained in the soft hulls of the four studied pistachio varieties was determined gravimetrically (Table 1). The highest oil content was extracted from the Akbari and Kalleh-Ghuchi varieties. Although the total oil and phenolic-compounds contents varied based on genotype, but the differences were neglectable and all the varieties contained around 5–7% oil. These records were comparable with those of the previous reports on solvent extraction of phenolic compounds from pistachio green hulls (Goli et al., 2005; Rajaei et al., 2010).

3.2. Comparison of FA profiles

The FA profile of the extracts and canola oil analyzed by GC are shown in Table 2. The major FFAs observed in all pistachio varieties included Lauric acid (C12:0), Myristic acid (C14:0), Palmitic acid (C16:0), Oleic acid (C18:1), Linolenic acid (C18:3), and Arachidic acid (C20:0).

Oleic acid (C18:1), a monounsaturated FA (MUFA), was the most dominant FA seen in all the samples. This was in line with the findings of the majority of studies conducted on edible or nonedible plant oil feedstocks (Saraf and Thomas, 2007; Atabani et al., 2013; Altun, 2014). However, significant differences were observed among the studied varieties of pistachio herein in terms of C18:1 content with Ahmad-Aghaei and Akbari PHEs possessing the highest and the lowest amounts, respectively. Moreover, an ideal semi-equal distribution of FAMEs could be observed in the PHEs of Kalleh-Ghuchi and Akbari, but the desirable 5:1 mass ratio of C18:1 and C14:0 suggested by Schenk et al. (2008) to achieve ideal biodiesel properties was only observed in the PHE obtained from Kalleh-Ghuchi variety.

It is worth mentioning that Arena et al. (2007) determined the FA composition (%) of the oil obtained from pistachio nuts found in different countries, i.e., Italy, Turkey, Iran, and Greece and all the investigated oil samples were characterized by high oleic acid contents (55–70%), showing a composition almost identical to that of olive oil. Similar observations were also made by Ryan et al. (2006) and Satil et al. (2003). On the contrary, based on the results obtained herein, the FAME profile of the investigated PHEs were not comparable with those of the pistachio nuts. The distinct differences in the FAME profiles of pistachio nuts and hulls have also been reported by previous studies (Chahed et al., 2006).

The saturation level of the PHE samples is presented in Table 2. The saturated fatty acids (SFAs) in the analyzed profiles included Lauric acid, Myristic acid, Palmitic acid, and Arachidic acid. FAME profile of the Akbari variety consisted of the highest SFAs (50%) with an SFA to unsaturated fatty acid (USFA) ratio of about 0.96. On the contrary, the lowest level of saturation was seen in the Ahmad-Aghaei PHE with an SFA to USFA ratio of 0.3. The ratio of MUFA to polyunsaturated fatty acids (PUFA) is also an important factor in determining the stability of a given oil feedstock for biodiesel production (Schenk et al., 2008). Ahmad-Aghaei variety had the highest MUFA to PUFA ratio (1.3) while Akbari variety had the lowest ratio of 0.38. Schenk et al. (2008) suggested that to achieve desirable biodiesel characteristics, an ideal FAME profile should be rich in MUFAs.

3.3. Bioprospecting of biodiesel properties based on FAME profiles

Among the PHEs investigated, Kalleh-Ghuchi PHE was found to possess the highest OS of 77.4 h and therefore, was added as antioxidant additive to the produced CBD as explained earlier (see Section 2.6). It has been well established that FA profile could directly influence quality parameters of the resultant biodiesel (Talebi et al., 2014). Minor alterations in the properties of CBD were observed in response to the addition of the antioxidant additive at its highest concentration, i.e., 10000 ppm (Table 3).

3.4. Enhancement of biodiesel oxidation stability using PHE as antioxidant

As mentioned earlier, the oil extracted from the soft hulls of Kalleh-Ghuchi pistachio variety was found to result in the highest IP. Therefore, this extract was added to CBD as antioxidant and was compared with the most frequently used biodiesel antioxidant, i.e., PG. It is worth quoting that different parts of pistachio including

Table 1
The physico-chemical properties of the extracted oil from the soft hull of important Iranian pistachio varieties.

Pistachio varieties	Total oil content (%dwt.)	Iodine value (IV) g I/100 g oil	Saponification value (SV) mg KOH/g	acid value (AV) mg KOH/g	Peroxide value (PV)	oil density g/ml	Oil viscosity (cP)	Color (in red, Lovibond)
Ahmad-Aghaei	$5.5 \pm 0.3^{A*}$	64.72 ± 2.3^{B}	164 ± 3.3^{A}	16 ± 1.5^{A}	0	$0.82 \pm .5^{A}$	1470 ± 42^{B}	0.25 ± 0.03^{B}
Fandoghi	5.2 ± 0.1^{A}	60.89 ± 1.9^{B}	178 ± 2.8^{B}	31 ± 1.6^{C}	0	0.89 ± 0.3^{B}	869 ± 52^{D}	0.30 ± 0.05^{B}
Kalleh-Ghuchi	6.8 ± 0.3^{B}	60.87 ± 2.1^{B}	193 ± 4.5^{C}	31 ± 2.1^{C}	0	0.94 ± 0.7^{C}	6029 ± 127^{A}	0.55 ± 0.06^{C}
Akbari	7.2 ± 0.3^{B}	44.00 ± 0.3^{A}	208 ± 5.1^{D}	22 ± 1.1^{B}	0	0.88 ± 0.4^{B}	1110 ± 42^{C}	0.1 ± 0.02^{A}

*Different letters show significantly different results ($P < 0.05$).

Table 2
Comparison of the fatty acid composition of the PHEs obtained from four commercially-important Iranian pistachio varieties.

Pistachio varieties	Fatty acid composition						
	C12:0	C14:0	C16:0	C18:1	C18:2	C18:3	SFA/USFA[a]
Ahmad-Aghaei	6.61 ± 0.47[b]	4.72 ± 0.49	12.13 ± 0.45	43.66 ± 0.66	7.73 ± 0.31	25.73 ± 1.12	0.30
Fandoghi	14.1 ± 0.46	10.09 ± 0.5	15.03 ± 0.34	30.93 ± 0.83	10.79 ± 0.21	19.18 ± 0.48	0.64
Kalleh-Ghuchi	21.05 ± 0.67	3.82 ± 0.51	16.81 ± 0.51	24.78 ± 0.69	14.43 ± 0.73	19.96 ± 0.59	0.70
Akbari	19.04 ± 0.29	15.78 ± 0.5	14.51 ± 0.19	14.15 ± 0.49	12.94 ± 0.49	24.22 ± 0.36	0.96
CBD[c]	ND	ND	5.33 ± 0.76	59.66 ± 0.65	20.40 ± 0.24	12.33 ± 0.36	0.06
CBD+ 10000 ppm PHE	ND	ND	5.87 ± 0.33	58.74 ± 1.17	20.12 ± 0.50	11.84 ± 0.66	0.06

ND: not determined.
[a] SFA/USFA: total saturated fatty acid to unsaturated fatty acid ratio.
[b] Data expressed as mean ± SD (n = 3).
[c] Canola biodiesel.

Table 3
Comparison of the estimated properties of canola biodiesel with (10000 ppm) and without the extracted oil from the soft hulls of the major Iranian pistachio variety, i.e., Kalleh-Ghuchi.

Sample	Biodiesel Properties										
	SV	IV	CN	DU	CFPP	CP	PP	APE	BAPE	HHV	ν	ρ
CBD	195.455	124.345	46.247	125.12	−14.802	−2.188	−9.197	125.12	45.06	38.587	3.602	0.86
CBD+ 10000 ppm PHE	193.265	121.67	47.165	122.66	−14.633	−1.904	−8.888	122.66	43.8	38.132	3.552	0.85

SV: Saponification value, IV: Iodine value, CN: Cetane number, DU: Degree of unsaturation, CFPP: Cold filter plugging point, CP: Cloud Point, PP: pour Point, APE: Allylic Position Equivalent, BAPE: Bis-AllylicPosition Equivalent, HHV: Higher Heating Value, ν: kinematic viscosity, ρ: Density. CBD: Canola Biodiesel.

hulls are rich in tocopherol and phytosterol, both acting as strong natural antioxidants (Ryan et al., 2006). Yoshida and Niki (2003) argued that phytosterol chemically acted as an antioxidant, like a radical scavenger, and prevented the oxidation of methyl linoleate in solution.

As revealed by the data presented in Fig. 2a, the OS of CBD was significantly increased by increasing the PHE concentration. More specifically, the OS of the investigated biodiesel was increased by more than four times in response to 5000 ppm PHE inclusion. The stabilization factor (F) data also proved the effectiveness of increasing PHE concentrations on the OS; for instance, the F_{10000} was about 500% higher than the F_{1000}. A linear correlation between the IP and the antioxidant concentration was also observed

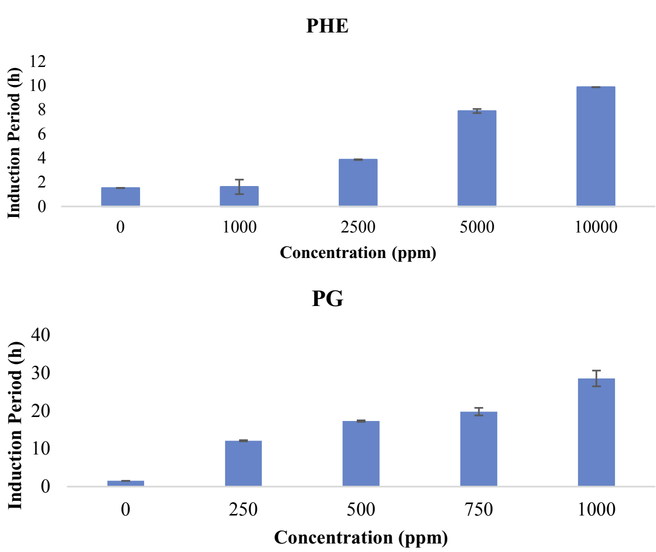

Fig. 2. Effect of antioxidants addition at various concentrations on the oxidation stability of neat canola biodiesel using rancimat at 20 L/h Air flow and 110 °C. A: Propyl Gallate (PG) and B: Pistachio hull extract (PHE) obtained from the major Iranian pistachio variety, i.e., Kalleh-Ghuchi.

($R^2 = 0.93$). Moreover, it was found that a concentration of 2500 ppm of PHE was sufficient to improve the IP of neat CBD (control) from 1.53 h to above 3 h as required by ASTM D6751-12 specification for biodiesel OS.

PG in the its lowest concentration of 250 ppm increased the OS to 12.11 h which was over the minimum standard requirement while also offering an effectiveness close to F_{10000} for Kalleh-Ghuchi PHE. Similar to the PHE, increasing the concentration of PG significantly increased the IP. More specifically, the highest investigated PG concentration of 1000 ppm enhanced the OS of CBD to 28.56 h (Fig. 2-b). This was in line with the results of the previously published reports indicating the higher effectiveness of synthetic antioxidants compared with natural antioxidants (Dunn, 2005; Focke et al., 2012; Fattah et al., 2014). For instance, improvements in the OS of peanut oil biodiesel were reported by the use of both natural/synthetic antioxidants, i.e., ethanol extract of green tea, α-tocopherol, and TBHQ by Pinto et al. (2015). They also stressed on the higher efficiency of the synthetic antioxidant, i.e., TBHQ.

In spite of the fact that higher concentrations of the bio-antioxidant, i.e., PHE, was required, its application would be justified by the probable health hazards of its synthetic counterpart. On the other hand, 23% of the global biodiesel production takes place in top pistachio producing countries where a huge deal of pistachio fresh hulls are generated (Fig. 3 and Table 4). Countries such as United States of America, Spain, China, Italy, Greece, and Turkey are located on the pistachio production belt and are among the top 10 pistachio producing countries in the world. For instance, it was estimated that pistachio production of the USA in the year 2017 amounted to 270 thousand tons, ranked as the second highest producer in the world (FAO, 2016), while the USA itself is the largest biodiesel producer in the world as well (EIA, 2014). Therefore, the soft pistachio hulls generated in large quantities in pistachio farms as waste can be purposefully valorized for natural antioxidant production.

Moreover, countries like Iran where a high deal of such pistachio waste is generated but no biodiesel production takes place at the moment (EIA, 2014), can invest on the valorization of this abundant

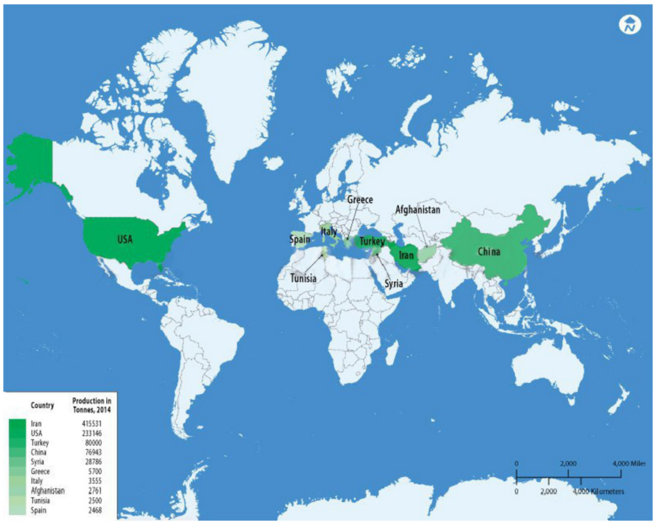

Fig. 3. Top pistachio producing countries in the world.

Table 4
Statistics showing the distribution of biodiesel production in the world and the share contributed by pistachio producing countries.

Rank	Country	Biodiesel production in 2014 (1000 bbl/d)
1	United State[a]	83
2	Brazil	59.66
3	Indonesia	58.76
4	Germany	56.56
5	Argentina	50.21
6	France	36.1
7	Thailand	20.45
8	Spain[a]	14.67
9	Poland	13.10
10	Netherland	12.17
11	China[a]	12.60
12	Belgium	11.73
13	Colombia	9.86
14	Malaysia	9.76
15	Italy[a]	6.75
16	Finland	6.49
17	United kingdom	6.30
18	Portugal	6.14
19	Canada	5.48
20	Korea South	5.28
21	Austria	4.69
22	Czech Republic	4.28
23	Denmark	3.91
24	Sweden	3.52
25	Greece[a]	3.3
⋮		
35	Turkey[a]	0.53
Total global production		**529**[b]

[a] Among top 10 pistachio producing countries (Fig. 3).
[b] 120.85 out of 529 (1000 barrel/d), i.e., ~ 23% of global biodiesel production takes place in top pistachio producing countries.

waste stream for the production of natural biodiesel antioxidants as added-value product. The final product could be exported enhancing the economic viability of pistachio farming in these countries while such a practice could also improve the environmental features of the pistachio farming.

3.5. Environmental considerations based on LCA

To investigate the environmental aspects of the developed scenarios, four damage categories were considered and the two scenarios were compared based on the indices calculated herein. A summary of the results obtained is presented in Table 5. As presented, in two damage categories (i.e., Climate change and Human health damage categories), Sc-1 dominated Sc-2 and proved to be more environmentally friendly.

The results of Climate change damage category clearly showed that Sc-1 could result in a negative total greenhouse gas (GHG) emission. Based on the results obtained, 1 kg of CBD supplemented with PHEs was responsible for −1.78E-01 kg $CO_{2,eq}$. In contrast to Sc-1, CBD added with PG imposed a positive burden on the environment and it accounted for 3.54E-01 kg $CO_{2,eq}$/kg biodiesel. In Sc-1 and Sc-2, 2500 mg PHEs and 250 mg PG were respectively added to 1 kg of CBD. In this context, the production of 2500 mg PHEs had a positive impact (negative GHG emissions) on Climate change damage category due to the hexane used in this process. Hexane production process leads to the production of two other co-products (i.e., Methylcyclohexane and Heptane). Considering these co-products as avoided products, hexane production process is the main reason behind this reduction potential. It should be highlighted that hexane has a fossil origin and is chiefly obtained by refining crude oil. Therefore, as long as the hexane employed in the PHE extraction process is recovered (recycled), its application will be more environmentally beneficial compared with the use of PG, in terms of GHG emissions. Overall, production and consumption of PHEs instead of PG as biodiesel additive had a positive environmental performance in terms of Climate change mitigation.

The second damage category evaluated herein was Human health damage category. The Human health damage category is composed of the following midpoints: “human toxicity”, “respiratory effects”, “ionizing radiation”, “ozone layer depletion”, and “photochemical oxidation” (Jolliet et al., 2003). Similar to the Climate change damage category, this category was also shown to have a more favorable environmental performance when CBD was supplemented with PHEs compared with PG. Accordingly; the burden imposed by Sc-2 was estimated to be 1.26% higher than that of Sc-1. The difference in biodiesel production and treatment stages of these scenarios was not significant but the most pronounced difference was observed in the antioxidant production stage. Sc-1 in the PHEs production stage offered a negative value of 6.05E-08 DALY/kg biodiesel because of the avoided products of the hexane production stage (i.e., Methylcyclohexane and Heptane).

Contrary to the two damage categories assessed, the outcomes of the other damage categories evaluated (i.e., Ecosystem quality and Resources) were not in favor of Sc-1. As shown, antioxidant production and consumption under the conditions of Sc-1 could not compete with Sc-2 in terms of Ecosystem quality damage category. Each kg of biodiesel prepared the under circumstances of Sc-1 resulted in 4.59E-02 PDF/m^2.yr which was approximately 4 times as much as that of Sc-2. Stage by stage evaluations proved that the highest negative impact was brought about by PHEs production stage followed by biodiesel production and treatment stages. Based on the results obtained herein, the negative impact of PHEs production stage on the Ecosystem quality damage category was approximately 86 times as much as that of the PG production stage.

The final damage category taken into account was Resources, referring to the primary resource requirements for an activity (or production) and the risk of resource depletion by mankind as an important issue for future generations (Rajaeifar et al., 2016). One kg of CBD prepared under the circumstances of Sc-1 required 8.86 MJ primary energy which was approximately 10% higher than the Sc-2 requirements. Similar to the other damage categories, the method by which the antioxidant was produced caused such a difference.

The LCA results obtained herein demonstrated that if climate

Table 5
Results of four damage categories achieved through the deployment of two scenarios[a].

Item	Unit	Pistachio hull processing	PHE/PG production	Biodiesel production & treatment	Grand total
Climate change					
Sc-1	kg $CO_{2,eq}$	6.65E-03	−4.45E-01	3.51E-01	−1.78E-01
Sc-2	kg $CO_{2,eq}$	–	1.35E-03	3.53E-01	3.54E-01
Human Health					
Sc-1	DALY	4.95E-09	−6.05E-08	3.95E-07	3.28E-07
Sc-2	DALY	–	1.09E-09	3.98E-07	3.99E-07
Ecosystem quality					
Sc-1	PDF/m^2.yr	9.33E-04	2.81E-02	1.08E-02	4.59E-02
Sc-2	PDF/m^2.yr	–	3.25E-04	1.08E-02	1.12E-02
Resources					
Sc-1	MJ primary	1.07E-01	5.69E-01	8.04E+00	8.86E+00
Sc-2	MJ primary	–	3.14E-02	8.09E+00	8.12E+00

[a] Sc-1: CBD supplemented with PHE and Sc-2: CBD supplemented with PG.

change mitigation objectives are the main goal as has been the case in numerous studies reported previously (Tabatabaie et al., 2018; Guerrero and Muñoz, 2018), PHEs production and consumption will outperform PG antioxidant production and consumption. This was also true if human health would be regarded as prominent. Such finding was in support of previous studies raising serious concerns about the safety of PG due to an association between this chemical and tumors in rats (Levy, 1982).

4. Conclusions

PG is the most promising synthetic antioxidant used to prevent oxidative degradation of biodiesel and increase its stability. However, its safety has been questioned owing to the health risks associated with its application as proposed by the National Toxicology Program (U.S. Department of Health and Human Services). Herein, the application of a naturally-found alternative to PG, i.e., PHEs in CBD was investigated. It was found that a concentration of 2500 ppm of PHE and 250 ppm of PG was needed to improve the IP of CBD from 1.53 h to above 3 h as required by ASTM D6751-12 (USA) specification for biodiesel OS. In spite of the fact that higher concentrations of the bio-antioxidant was required, its application would be justified by the probable health hazards of its synthetic counterparts. On the other hand, 23% of the global biodiesel production takes place in top pistachio producing countries where a huge amount of pistachio fresh hulls are generated. Therefore, valorization of this considerable agro-waste stream into PHE seems like a promising strategy to enhance the favorable environmental and human health aspects of biodiesel. Moreover, it was also revealed that PHEs production and applications were in line with climate change mitigation objectives.

References

Agarwal, A.K., Khurana, D., Dhar, A., 2015. Improving oxidation stability of biodiesels derived from Karanja, Neem and Jatropha: step forward in the direction of commercialisation. J. Clean. Prod. 107, 646–652.

Altun, Ş., 2014. Effect of the degree of unsaturation of biodiesel fuels on the exhaust emissions of a diesel power generator. Fuel 117, 450–457.

AOCS, 1999. Official Methods and Recommended Practices. AOCS Press, Champaign.

Arena, E., Campisi, S., Fallico, B., Maccarone, E., 2007. Distribution of fatty acids and phytosterols as a criterion to discriminate geographic origin of pistachio seeds. Food Chem. 104 (1), 403–408.

Atabani, A.E., Silitonga, A.S., Ong, H.C., Mahlia, T.M.I., Masjuki, H.H., Badruddin, I.A., Fayaz, H., 2013. Non-edible vegetable oils: a critical evaluation of oil extraction, fatty acid compositions, biodiesel production, characteristics, engine performance and emissions production. Renew. Sustain. Energy Rev. 18, 211–245.

Bohluli, G., 2006. Chemical Composition and Digestability of Pistachio Byproducts and Their Effects on Holstein Cows'nutrition. Ferdowsi University of Mashhad, Iran.

Botella, L., Bimbela, F., Martín, L., Arauzo, J., Sánchez, J.L., 2014. Oxidation stability of biodiesel fuels and blends using the Rancimat and PetroOXY methods. Effect of 4-allyl-2, 6-dimethoxyphenol and catechol as biodiesel additives on oxidation stability. Front. Chem. 2.

Cavalett, O., Chagas, M.F., Seabra, J.E., Bonomi, A., 2013. Comparative LCA of ethanol versus gasoline in Brazil using different LCIA methods. Int. J. Life Cycle Assess. 18 (3), 647–658.

Chahed, T., Hamrouni, I., Dhifi, W., Msaada, K., Kchouk, M.E., Marzouk, B., 2006. Lipid evaluation during the development of pistachio seed from the region of Kairouan (Middle of Tunisia). J. Food Lipids 13 (4), 375–389.

Christensen, E., McCormick, R.L., 2014. Long-term storage stability of biodiesel and biodiesel blends. Fuel Process. Technol. 128, 339–348.

Cornelius, J.A., 1977. International standards for palm oil. J. Am. Oil Chem. Soc. 54 (12), A943–A950.

de Sousa, L.S., de Moura, C.V.R., de Oliveira, J.E., de Moura, E.M., 2014. Use of natural antioxidants in soybean biodiesel. Fuel 134, 420–428.

Du Plessis, L.M., De Villiers, J.B.M., Van der Walt, W.H., 1985. Stability studies on methyl and ethyl fatty acid esters of sunflower seed oil. JAOCS (J. Am. Oil Chem. Soc.) 62 (4), 748–752.

Dunn, R.O., 2005. Effect of antioxidants on the oxidative stability of methyl soyate (biodiesel). Fuel Process. Technol. 86 (10), 1071–1085.

Energy Information Administration (EIA), 2014. Biodiesel Production Statistics.

FAO, 2016. Food and Agriculture Organization of the United Nations.

Farzad, S., Mandegari, M.A., Görgens, J.F., 2017. Integrated techno-economic and environmental analysis of butadiene production from biomass. Bioresour. Technol. 239, 37–48.

Fattah, I.R., Masjuki, H.H., Kalam, M.A., Hazrat, M.A., Masum, B.M., Imtenan, S., Ashraful, A.M., 2014. Effect of antioxidants on oxidation stability of biodiesel derived from vegetable and animal based feedstocks. Renew. Sustain. Energy Rev. 30, 356–370.

Focke, W.W., van der Westhuizen, I., Grobler, A.L., Nshoane, K.T., Reddy, J.K., Luyt, A.S., 2012. The effect of synthetic antioxidants on the oxidative stability of biodiesel. Fuel 94, 227–233.

Goli, A.H., Barzegar, M., Sahari, M.A., 2005. Antioxidant activity and total phenolic compounds of pistachio (*Pistachia vera*) hull extracts. Food Chem. 92 (3), 521–525.

Guerrero, A.B., Muñoz, E., 2018. Life cycle assessment of second generation ethanol derived from banana agricultural waste: environmental impacts and energy balance. J. Clean. Prod. 174, 710–717.

ISO, 2006. Technical Committee ISO/TC 207 EmSS, Life Cycle Assessment. Environmental Management: Life Cycle Assessment: Principles and Framework. ISO.

Jolliet, O., Margni, M., Charles, R., Humbert, S., Payet, J., Rebitzer, G., Rosenbaum, R., 2003. IMPACT 2002+: a new life cycle impact assessment methodology. Int. J. Life Cycle Assess. 8 (6), 324.

JRC, I., 2010. Handbook—general Guide for Life Cycle Assessment—detailed Guidance. Publication Office of the European Union, Luxembourg.

Kamal-Eldin, A., Pokorný, J., 2005. Analysis of Lipid Oxidation, vol. 1. AOCS Press, Champaign.

Khoshnevisan, B., Rafiee, S., Tabatabaei, M., Ghanavati, H., Mohtasebi, S.S., Rahimi, V., Karimi, K., 2017. Life cycle assessment of castor-based biorefinery: a well to wheel LCA. Int. J. Life Cycle Assess. 1–18.

Khoshnevisan, B., Tsapekos, P., Alvarado-Morales, M., Rafiee, S., Tabatabaei, M., Angelidaki, I., 2018. Life cycle assessment of different strategies for energy and nutrient recovery from source sorted organic fraction of household waste. J. Clean. Prod. 180, 360–374.

Kumar, S., Kumar, R., Kumar, M., 2018. Experimental investigations of oxidation stability of biodiesel produced from Prunus armeniaca oil (apricot oil) and effect of various antioxidants on stability, engine performance and emissions. Fuel 216, 861–869.

Levy, M., 1982. Carciogenesis Bioassay of Propyl Gallate (Program NT).

Machado, Y.L., Neto, A.D., Fonseca, J.L.C., Dantas, T.N.C., 2014. Antioxidant stability in vegetable oils monitored by the ASTM D7545 method. J. Am. Oil Chem. Soc. 91 (7), 1139–1145.

Mandegari, M.A., Farzad, S., Görgens, J.F., 2017a. Economic and environmental assessment of cellulosic ethanol production scenarios annexed to a typical sugar mill. Bioresour. Technol. 224, 314–326.

Mandegari, M.A., Farzad, S., van Rensburg, E., Görgens, J.F., 2017b. Multi-criteria Analysis of a Biorefinery for Co-production of Lactic Acid and Ethanol from Sugarcane Lignocellulose. Biofuels, Bioproducts and Biorefining. https://doi.org/10.1002/bbb.1801.

Melamu, R., Von Blottnitz, H., 2011. 2nd Generation biofuels a sure bet? A life cycle assessment of how things could go wrong. J. Clean. Prod. 19 (2), 138–144.

Metcalfe, L.D., Schmitz, A.A., Pelka, J.R., 1966. Rapid preparation of fatty acid esters from lipids for gas chromatographic analysis. Anal. Chem. 38, 514–515.

Mittelbach, M., Schober, S., 2003. The influence of antioxidants on the oxidation stability of biodiesel. J. Am. Oil Chem. Soc. 80 (8), 817–823.

Pinto, L.M., de Souza, A.L., Souza, A.G., Santos, I.M., Queiroz, N., 2015. Comparative evaluation of the effect of antioxidants added into peanut (*Arachis hypogae* l.) oil biodiesel by P-DSC and rancimat. J. Therm. Anal. Calorim. 120 (1), 277–282.

Pölczmann, G., Tóth, O., Beck, Á., Hancsók, J., 2016. Investigation of storage stability of diesel fuels containing biodiesel produced from waste cooking oil. J. Clean. Prod. 111, 85–92.

Rafiee, S., Khoshnevisan, B., Mohammadi, I., Aghbashlo, M., Clark, S., 2016. Sustainability evaluation of pasteurized milk production with a life cycle assessment approach: an Iranian case study. Sci. Total Environ. 562, 614–627.

Rajaei, A., Barzegar, M., Mobarez, A.M., Sahari, M.A., Esfahani, Z.H., 2010. Antioxidant, anti-microbial and antimutagenicity activities of pistachio (*Pistachia vera*) green hull extract. Food Chem. Toxicol. 48 (1), 107–112.

Rajaeifar, M.A., Abdi, R., Tabatabaei, M., 2017. Expanded polystyrene waste application for improving biodiesel environmental performance parameters from life cycle assessment point of view. Renew. Sustain. Energy Rev. 74, 278–298.

Rajaeifar, M.A., Akram, A., Ghobadian, B., Rafiee, S., Heijungs, R., Tabatabaei, M., 2016. Environmental impact assessment of olive pomace oil biodiesel production and consumption: a comparative lifecycle assessment. Energy 106, 87–102.

Ryan, E., Galvin, K., O'connor, T.P., Maguire, A.R., O'brien, N.M., 2006. Fatty acid profile, tocopherol, squalene and phytosterol content of Brazil, pecan, pine, pistachio and cashew nuts. Int. J. Food Sci. Nutr. 57 (3–4), 219–228.

Saraf, S., Thomas, B., 2007. Influence of feedstock and process chemistry on biodiesel quality. Process Saf. Environ. Protect. 85 (5), 360–364.

Serrano, M., Martínez, M., Aracil, J., 2013. Long term storage stability of biodiesel: influence of feedstock, commercial additives and purification step. Fuel Process. Technol. 116, 135–141.

Satil, F., Azcan, N., Baser, K.H.C., 2003. Fatty acid composition of pistachio nuts in Turkey. Chem. Nat. Comp. 39 (4), 322–324.

Schenk, P.M., Thomas-Hall, S.R., Stephens, E., Marx, U.C., Mussgnug, J.H., Posten, C., Kruse, O., Hankamer, B., 2008. Second generation biofuels: high-efficiency microalgae for biodiesel production. Bioenergy Res. 1 (1), 20–43.

Shantha, N.C., Decker, E.A., 1994. Rapid, Sensitive, Iron-based Spectrophotometric Methods for Determination of Perorlride Values of Food Lipids.

Talebi, A.F., Mohtashami, S.K., Tabatabaei, M., Tohidfar, M., Bagheri, A., Zeinalabedini, M., Hadavand Mirzaei, H., Mirzajanzadeh, M., Malekzadeh Shafaroudi, S., Bakhtiari, S., 2013. Fatty acids profiling: a selective criterion for screening microalgae strains for biodiesel production. Algal Res. 2 (3), 258–267.

Talebi, A.F., Tabatabaei, M., Chisti, Y., 2014. BiodieselAnalyzer: a user-friendly software for predicting the properties of prospective biodiesel. Biofuel Res. J. 1 (2), 55–57.

Talebi, A.F., Tohidfar, M., Mousavi Derazmahalleh, S.M., Sulaiman, A., Baharuddin, A.S., Tabatabaei, M., 2015. Biochemical modulation of lipid pathway in microalgae Dunaliella sp. for biodiesel production. BioMed Res. Int. 2015.

Tabatabaie, S.M.H., Tahami, H., Murthy, G.S., 2018. A regional life cycle assessment and economic analysis of camelina biodiesel production in the Pacific Northwestern US. J. Clean. Prod. 172, 2389–2400.

United Nations Environment Programme (UNDP), 2009. Biofuels working group, & united Nations environment Programme. In: International Panel for Sustainable Resource Management. Towards Sustainable Production and Use of Resources: Assessing Biofuels. UNEP/Earthprint.

Veleva, V., Ellenbecker, M., 2001. Indicators of sustainable production: framework and methodology. J. Clean. Prod. 9 (6), 519–549.

Yoshida, Y., Niki, E., 2003. Antioxidant effects of phytosterol and its components. J. Nutr. Sci. Vitaminol. 49 (4), 277–280.

Yunos, N.S.H.M., Chu, C.J., Baharuddin, A.S., Mokhtar, M.N., Sulaiman, A., Rajaeifar, M.A., Nabavi Larimi, Y., Talebi, A.H., Mohammed, M.A.P., Aghbashlo, M., Tabatabaei, M., 2017. Enhanced oil recovery and lignocellulosic quality from oil palm biomass using combined pretreatment with compressed water and steam. J. Clean. Prod. 142, 3834–3849.